The Nature of Excess Electrons in Anatase and Rutile from hybrid DFT and RPA

Supplementary Information

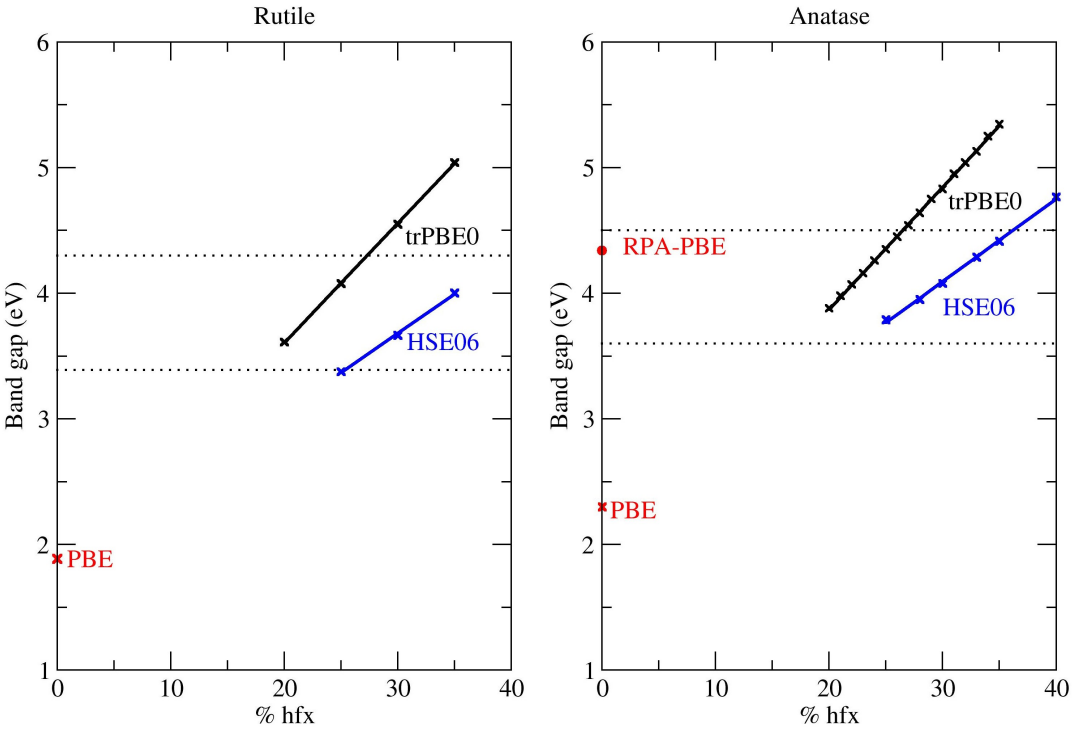
Clelia Spreafico,[a] and Joost VandeVondele *[a]

[a] *Nanoscale Simulations, Department of Materials, ETH Zürich, Wolfgang-Pauli-Str. 27, CH-8093 Zürich, Switzerland. E-mail:Joost.VandeVondele@mat.ethz.ch*

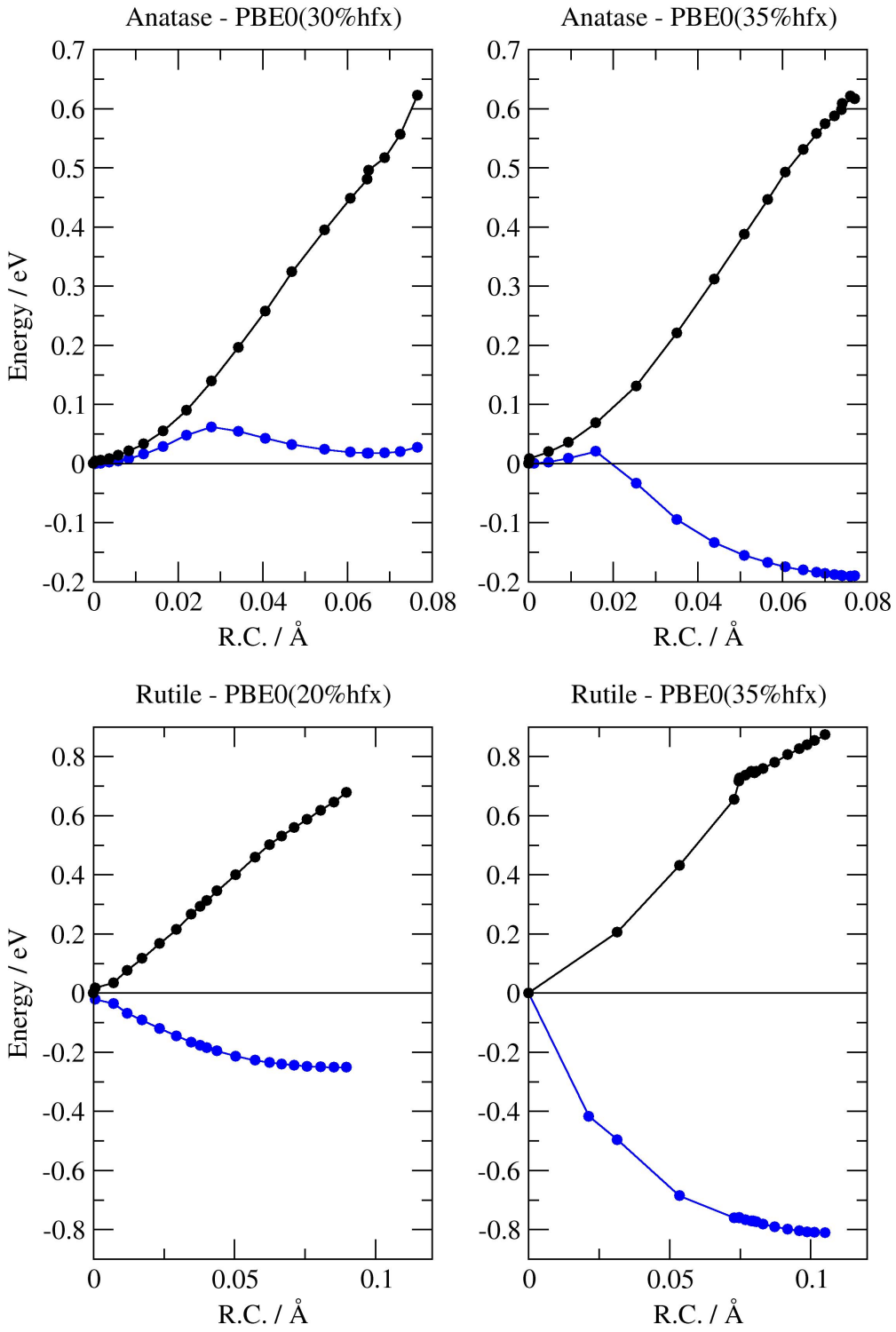
S 1 Cell parameters and inter atomic distances for rutile and anatase, adopting PBE, HSE06 and tr-PBE0 functionals.

	Anatase		
	a/Å	*c*/Å	Ti-O distance/Å
Experimental [1]	3.782	9.502	1.9322 ; 1.9788
PBE	3.804(+0.5%)	9.620(+1.2%)	1.944(+0.6%) ; 2.011(+1.7%)
HSE06	3.783(+0.0%)	9.469(-0.3%)	1.931(-0.1%) ; 1.975(-0.2%)
tr-PBE0 (20%hfx)	3.775(-0.2%)	9.581(+0.8%)	1.931(-0.1%) ; 1.989(+0.5%)
tr-PBE0 (25%hfx)	3.769(-0.3%)	9.561(+0.6%)	1.928(-0.2%) ; 1.983(+0.2%)
	Rutile		
	a/Å	*c*/Å	Ti-O distance/Å
Experimental [1]	4.587	2.954	1.946 ; 1.976
PBE	4.642(+1.2%)	2.971(+0.6%)	1.961(+0.7%) ; 2.010(+1.5%)
HSE06	4.591(+0.1%)	2.955(+0.0%)	1.945(-0.1%) ; 1.982(+0.3%)
tr-PBE0 (20%hfx)	4.596(+0.2%)	2.954(+0.0%)	1.944(-0.1%) ; 1.985(+0.4%)
tr-PBE0 (25%hfx)	4.585(+0.0%)	2.951(-0.1%)	1.941(-0.2%) ; 1.980(+0.2%)

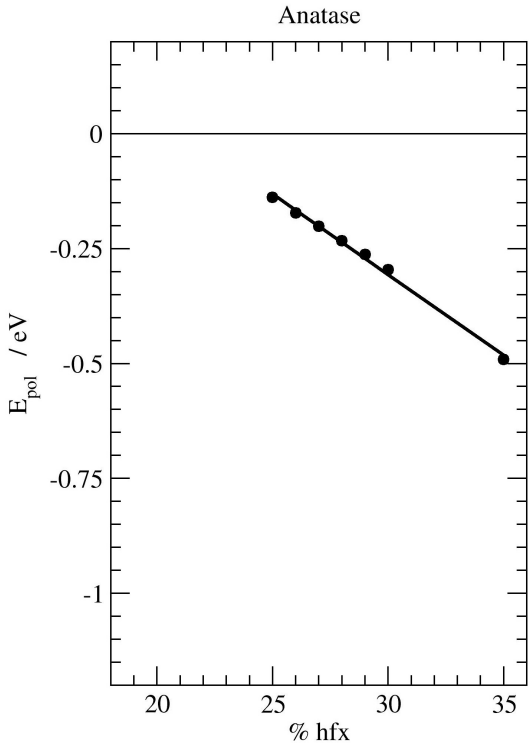
S 2 Band Gap of anatase and rutile, for different functionals and increasing amounts of %hfx. Black: PBE0. Blue: HSE06. Red, cross : PBE. Red, circle : RPA-PBE. Dotted lines enclose the band gap values reported in literature for hybrid DFT and GW calculations (taken from ref. [3]). The anatase DFT-RPA band gap is calculated according to the formula[2] : $E_{gap} = E(N+1) + E(N-1) - 2E(N)$, where $E(N)$ is the total energy of the $N-$electron system. The DFT-RPA band gap value is close to the 4.29 eV value reported for G_0W_0 calculations[3].



S 3 Blue curves: NEB profiles for the delocalized-localized transition in anatase and rutile with one excess electron, obtained with the truncated PBE0 functional and different amounts of %hfx. Black curves: Energetic cost of the corresponding lattice deformation as obtained for the neutral system.
R.C. = $d(Ti_c - O_{eq})_{Nth\ replica} - d(Ti_c - O_{eq})_{perfect\ lattice}$.



S 4 Polaron trapping energy (E_{pol}) for the anatase $6 \times 6 \times 2$ system, treated with the HSE functional and varying amounts of exact exchange. $\omega = 0.11 a_0$



S 5 Energy difference between a polaronic and delocalized geometry in presence of an excess electron ($\Delta E = E_{loc} - E_{deloc}$), for a provided polaron geometry. Employed is a small anatase $3 \times 3 \times 1$ system, to facilitate benchmarking and comparing different functionals, basis sets and codes. Negative values indicate stable polaron geometries, positive values indicate metastable polaron geometries. Relevant parameters for the QUANTUM ESPRESSO calculations are also given. Due to the computational cost, convergence of the QUANTUM ESPRESSO data is at the $10^{-3} E_H$ level. Details for the CP2K calculations are given in Section 2 of the manuscript and additional parameters can be found in **S** 12. All employed Gaussian basis sets for Ti and O are reported in **S** 13.

CP2K [4]		
BASIS_SET	FUNCTIONAL	$\Delta E/eV$
cc-TZ	tr-PBE0(40% hfx)	-0.49
	tr-PBE0(25% hfx)	0.23
	B3LYP(20% hfx)	1.20
ADMM *cc-TZ*	tr-PBE0(40% hfx)	-0.49
	tr-PBE0(25% hfx)	0.22
	B3LYP(20% hfx)	1.21
Ti_86-411(d31)G and *O_8-411d1* [5,6]	tr-PBE0(25% hfx)	0.25
	B3LYP(20% hfx)	0.84

QUANTUM ESPRESSO [7]		
exxdiv_treatment	FUNCTIONAL	$\Delta E/eV$
'vcut_spherical'	PBE0(25% hfx)	0.29
'gygi-baldereschi'	PBE0(25% hfx)	0.27
'vcut_spherical'	B3LYP(20% hfx)	0.92
'gygi-baldereschi'	B3LYP(20% hfx)	0.87
Simulation Parameters		
ecutwfc		150
ecutfock		400
conv_thr		1d-6
mixing_beta		0.3

Polaron Geometry in the anatase $3 \times 3 \times 1$ system. a=11.346 Å; c=9.502Å.

Ti	0.0025580316	0.0026559143	-0.0002149987	O	-1.8910562807	-0.0027072522	-0.4068640396
Ti	-1.8910161929	0.0015610421	-2.3746142108	O	-0.0009518779	0.0002961501	-1.9729439413
O	-1.8909875514	-0.0025021967	-4.3505404797	O	-1.8910416278	1.8837526566	-2.7884960589
Ti	-1.8910334392	1.8895215922	-4.7550348487	O	-0.0069896011	1.8845646264	0.4038764064
Ti	0.0019311757	1.8970224802	2.3717499162	O	0.0003113760	-0.0009116129	1.9725571793
O	-0.0018841752	1.8892814108	-5.1572484519	O	-1.8910287658	1.8905906597	2.7758025265
Ti	-3.7848574170	0.0026367202	-0.0001881534	O	-5.6666009105	-0.0069763764	-0.4039017774
Ti	-5.6790426317	0.0019492948	-2.3718589956	O	-3.7811409057	0.0002820560	-1.9728859211
O	-5.6713174719	-0.0018542444	-4.3448381777	O	-5.6700597532	1.8877883976	-2.7811315187
Ti	-5.6781676902	1.8960493123	-4.7512420700	O	-3.7750833967	1.8845229770	0.4037965885
Ti	-3.7839610156	1.8970347517	2.3717028577	O	-3.7823221399	-0.0008872548	1.9725838955
O	-3.7801578087	1.8892704776	-5.1573037736	O	-5.6698577863	1.8880692758	2.7806653123
Ti	3.7818542920	0.0050807951	0.0260017606	O	1.8845489924	-0.0069636732	-0.4039010805
Ti	1.8971103221	0.0020217673	-2.3718795568	O	3.7819875638	0.0009715541	-1.9681514320
O	1.8893052443	-0.0018970290	-4.3448270300	O	1.8880698897	1.8878391909	-2.7811105769
Ti	1.8961230958	1.8960569063	-4.7512304117	O	3.7819957469	1.8226297036	0.4458783777
Ti	3.7819969547	1.8952277202	2.3649087240	O	3.7819049825	-0.0174814468	2.0041894463
O	3.7819927160	1.8862044145	-5.1433151355	O	1.8878649938	1.8880242605	2.7806552400
Ti	0.0053411056	3.7819305704	-0.0264424090	O	-1.8910153123	3.7819830258	-0.4282066298
Ti	-1.8910306328	3.7820205324	-2.3873005650	O	-0.0173389942	3.7820223707	-2.0047909846
O	-1.8910338632	3.7820114904	-4.3601090754	O	-1.8910222058	-5.6657533019	-2.7885183890
Ti	-1.8910366767	-5.6716517281	-4.7550678345	O	-0.0069599986	-5.6666200185	0.4038772164
Ti	0.0019203782	-5.6791089288	2.3717281247	O	0.0009927040	3.7819559123	1.9677181358
O	-0.0019012861	-5.6713003804	-5.1572887630	O	-1.8910215926	-5.6727084817	2.7757859237
Ti	-3.7873317943	3.7819256123	-0.0263928400	O	-5.6047249969	3.7820713519	-0.4461815221
Ti	-5.6772508681	3.7820705380	-2.3652673668	O	-3.7646830838	3.7820001167	-2.0047625153
O	-5.6681518057	3.7819790767	-4.3588301878	O	-5.6700618523	-5.6698549249	-2.7811672753
Ti	-5.6782062862	-5.6782267597	-4.7512537750	O	-3.7750836494	-5.6666246561	0.4038219520
Ti	-3.7839683604	-5.6791007234	2.3716926817	O	-3.7829612545	3.7819690907	1.9677503249
O	-3.7801540751	-5.6713073363	-5.1573382449	O	-5.6699060915	-5.6701424604	2.7806423633
Ti	3.7820108000	3.7816545651	-0.0003223424	O	1.8227197827	3.7819639643	-0.4461763688
Ti	1.8952301562	3.7820710980	-2.3652175758	O	3.7819903694	3.7820172616	-2.0076247081
O	1.8861325543	3.7819571443	-4.3588314222	O	1.8879621090	-5.6698309128	-2.7811711410
Ti	1.8961160442	-5.6782320190	-4.7512748296	O	3.7820194855	-5.6048715046	0.4458212414
Ti	3.7819778116	-5.6773370780	2.3648928940	O	3.7820132088	3.7818522548	2.0068451024
O	3.7819717584	-5.6682082002	-5.1432662265	O	1.8878912096	-5.6701222061	2.7806111961
Ti	0.0026143006	-3.7847644157	-0.0002117501	O	-1.8910269616	-3.7793761113	-0.4068652455
Ti	-1.8910267823	-3.7835219198	-2.3745711963	O	-0.0009433189	-3.7823346571	-1.9729261465
O	-1.8910114982	-3.7794839131	-4.3505615493	O	-1.8910338518	-1.8910087590	-2.7802928542
Ti	-1.8910814259	-1.8910736587	-4.7510894454	O	-0.0026596379	-1.8910272713	0.4066968323
Ti	0.0014870805	-1.8910405846	2.3744560408	O	0.0003583381	-3.7811449127	1.9725553312
O	-0.0024939524	-1.8910092543	-5.1515312524	O	-1.8910114119	-1.8910611269	2.7800441586
Ti	-3.7847371081	-3.7847520400	-0.0001992387	O	-5.6665698406	-3.7750925296	-0.4040014844
Ti	-5.6790707703	-3.7838964954	-2.3718999267	O	-3.7811433540	-3.7823418100	-1.9729108720
O	-5.6713629530	-3.7801406877	-4.3449012792	O	-5.6726989861	-1.8910405778	-2.7761303085
Ti	-5.6716696386	-1.8910672658	-4.7473959825	O	-3.7793633982	-1.8910345626	0.4066800280
Ti	-3.7834350375	-1.8910067904	2.3743676703	O	-3.7822784265	-3.7811379840	1.9725785800
O	-3.7794889766	-1.8910016911	-5.1515935633	O	-5.6657588777	-1.8910500233	2.7880349384
Ti	3.7819647779	-3.7876431789	0.0258696194	O	1.8845364274	-3.7751288733	-0.4039192787
Ti	1.8970391658	-3.7838715646	-2.3718499659	O	3.7819750027	-3.7830106515	-1.9682313075
O	1.8893206389	-3.7801774927	-4.3448301970	O	1.8906368455	-1.8910011259	-2.7761678014
Ti	1.8895851891	-1.8911229384	-4.7474088895	O	3.7819594942	-1.8910796020	0.4276243171
Ti	3.7820415467	-1.8910958588	2.3868650305	O	3.7819276139	-3.7648206735	2.0040485555
O	3.7820131777	-1.8909677180	-5.1421244992	O	1.8837974529	-1.8911001418	2.7879885021

Delocalized Electron Geometry in the anatase $3 \times 3 \times 1$ system. a=11.346 Å; c=9.502Å.

Ti	-0.0000411545	0.0001037477	-0.0001222571	O	-1.8911035908	0.0000095698	-0.3959559709
Ti	-1.8912780734	-0.0001428054	-2.3754422110	O	-0.0000334021	-0.0000036992	-1.9796463824
O	-1.8909524165	-0.0000530705	-4.3552514036	O	-1.8909302860	1.8909998305	-2.7715030371
Ti	-1.8908249516	1.8908268052	-4.7510648659	O	0.0000218230	1.8910256677	0.3956996306
Ti	0.0000898155	1.8912686623	2.3752913551	O	-0.0000165494	0.0000574817	1.9795103805
O	0.0000127013	1.8910915999	-5.1468965075	O	-1.8910204297	1.8910224139	2.7714076050
Ti	-3.7819651497	0.0000840265	0.0005366027	O	-5.6728835598	0.0000601236	-0.3958732939
Ti	-5.6727149945	-0.0001655343	-2.3753539347	O	-3.7820065917	0.0000455549	-1.9796652658
O	-5.6730331328	-0.0000939516	-4.3551630243	O	-5.6730647784	1.8909927852	-2.7714929013
Ti	-5.6730932255	1.8908350915	-4.7510684520	O	-3.7819810401	1.8910748256	0.3957479701
Ti	-3.7819843276	1.8912643510	2.3756274175	O	-3.7819954684	0.0000150974	1.9797908911
O	-3.7819773711	1.8909692338	-5.1470568220	O	-5.6730110826	1.8909943405	2.7714031682
Ti	3.7820422817	0.0001004325	-0.0001172515	O	1.8910008826	0.0000089751	-0.3957775431
Ti	1.8910038009	-0.0001327780	-2.3752569724	O	3.7819733704	0.0000765109	-1.9796789785
O	1.8910544514	-0.0000262847	-4.3551421916	O	1.8910573750	1.8909249288	-2.7715632662
Ti	1.8909952623	1.8907692428	-4.7509313163	O	3.7819843049	1.8910930365	0.3958183539
Ti	3.7818876589	1.8912776068	2.3753564912	O	3.7820098144	-0.0000041151	1.9795208944
O	3.7819686202	1.8910600892	-5.1468193468	O	1.8909631868	1.8912234071	2.7711872734
Ti	-0.0000570761	3.7819579868	-0.0004081789	O	-1.8909999516	3.7820517273	-0.3962174791
Ti	-1.8912704245	3.7820265343	-2.3760883414	O	-0.0000525137	3.7820209741	-1.9796681243
O	-1.8909655822	3.7819823784	-4.3553801654	O	-1.8909395609	-5.6729499200	-2.7714453854
Ti	-1.8908389053	-5.6728384786	-4.7509823086	O	-0.0000375768	-5.6730770918	0.3955473595
Ti	0.0001043107	-5.6732005636	2.3751066169	O	0.0000996072	3.7819785300	1.9798664702
O	0.0000112854	-5.6730908236	-5.1470849355	O	-1.8909805256	-5.6730213808	2.7715030939
Ti	-3.7818676685	3.7820015121	0.0001072659	O	-5.6727953879	3.7819673103	-0.3961134354
Ti	-5.6727060793	3.7820213838	-2.3759746474	O	-3.7819856709	3.7819468009	-1.9797388024
O	-5.6731262478	3.7819918333	-4.3553036271	O	-5.6730998017	-5.6729481285	-2.7714824179
Ti	-5.6730981813	-5.6728346077	-4.7510404967	O	-3.7819776319	-5.6730521866	0.3957400343
Ti	-3.7819512572	-5.6732662713	2.3756035072	O	-3.7819679006	3.7819913126	1.9799423196
O	-3.7819835469	-5.6729657885	-5.1470708789	O	-5.6730145736	-5.6729859491	2.7714159289
Ti	3.7821360514	3.7819948472	-0.0006170755	O	1.8909815628	3.7820236802	-0.3960699410
Ti	1.8909629293	3.7820009044	-2.3759135225	O	3.7819924327	3.7819853732	-1.9798598642
O	1.8910512364	3.7819913386	-4.3552347532	O	1.8910985216	-5.6729191284	-2.7714779879
Ti	1.8909967029	-5.6727738604	-4.7508295760	O	3.7819933200	-5.6730872724	0.3957925872
Ti	3.7818761198	-5.6732461432	2.3753307982	O	3.7818996305	3.7819945137	1.9796990038
O	3.7819692400	-5.6730565461	-5.1468426177	O	1.8909354932	-5.6732240389	2.7713238743
Ti	-0.0000362683	-3.7820886953	-0.0000066284	O	-1.8910699132	-3.7820364316	-0.3959672456
Ti	-1.8912767855	-3.7818004119	-2.3754514945	O	-0.0000397593	-3.7820171680	-1.9795471275
O	-1.8909629687	-3.7819307600	-4.3552719767	O	-1.8909109519	-1.8909814689	-2.7713084358
Ti	-1.8907994234	-1.8910019113	-4.7512789823	O	-0.0000069825	-1.8909944411	0.3958104157
Ti	0.0000739638	-1.8909322898	2.3751245943	O	-0.0000345436	-3.7819018763	1.9796784093
O	-0.0000560035	-1.8910137457	-5.1468837106	O	-1.8909633711	-1.8910024809	2.7714212395
Ti	-3.7819543404	-3.7820482949	0.0005269688	O	-5.6728802745	-3.7820542956	-0.3958667962
Ti	-5.6727162792	-3.7817966628	-2.3753453548	O	-3.7820050714	-3.7820344943	-1.9796675767
O	-5.6730318301	-3.7819024891	-4.3551659798	O	-5.6729674670	-1.8909897377	-2.7713681789
Ti	-5.6731808573	-1.8910138518	-4.7513866191	O	-3.7819832090	-1.8909919304	0.3958403586
Ti	-3.7819564061	-1.8910066630	2.3755449592	O	-3.7820041771	-3.7820215604	1.9797879601
O	-3.7819991970	-1.8909976624	-5.1470776178	O	-5.6730209335	-1.8910019819	2.7713098676
Ti	3.7820301087	-3.7820724987	-0.0001277204	O	1.8909927122	-3.7819903153	-0.3958144735
Ti	1.8909965987	-3.7818319536	-2.3752716992	O	3.7819656066	-3.7820657042	-1.9796780194
O	1.8910674259	-3.7819320742	-4.3551804793	O	1.8910440560	-1.8909984516	-2.7715296067
Ti	1.8909724017	-1.8910068913	-4.7512656230	O	3.7820004615	-1.8909978697	0.3958565640
Ti	3.7819801339	-1.8910012857	2.3751913547	O	3.7820237845	-3.7819858409	1.9795307180
O	3.7819659793	-1.8910116294	-5.1467846754	O	1.8910007589	-1.8910149368	2.7712574898

S 6 Variation in the inter atomic distance (in Å) between the electron localization center, Ti_c, and its nearest neighbors, as a function of the amount of exact exchange in the tr-PBE0 functional.

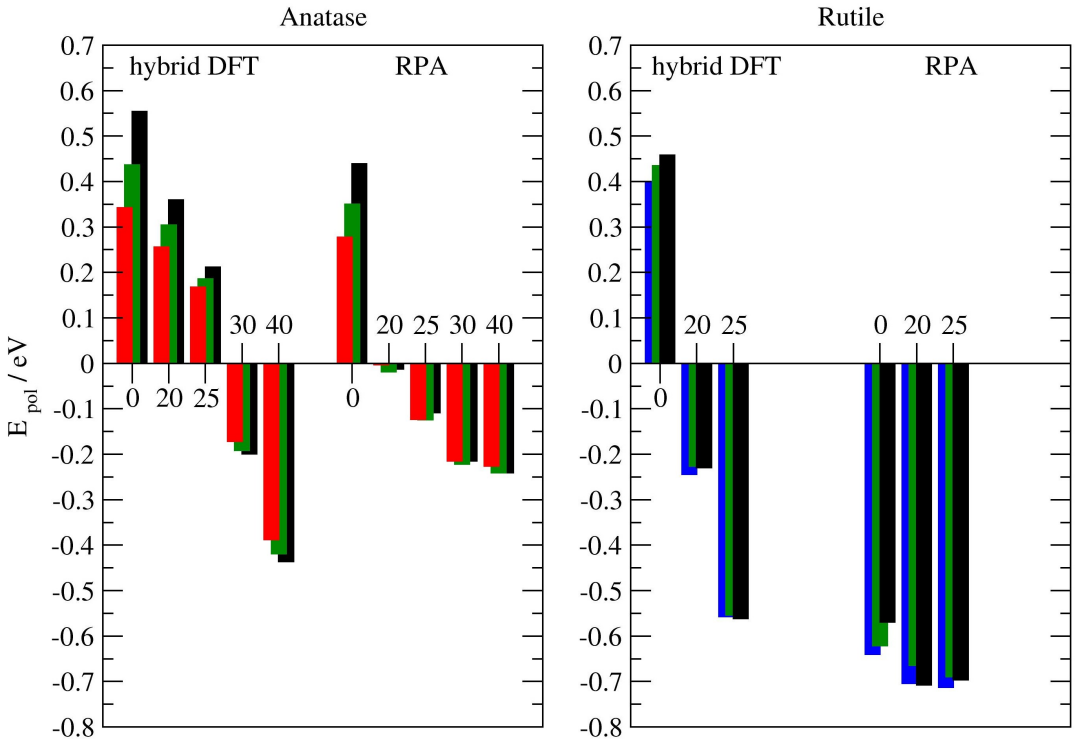
		Anatase		
% hfx	$Ti_c - O$ eq	$Ti_c - O$ ax	$Ti_c - Ti$ eq	$Ti_c - Ti$ ax
25	6.22E-02	2.69E-02	-1.48E-02	-1.19E-02
26	6.25E-02	2.73E-02	-1.51E-02	-1.18E-02
27	6.91E-02	3.20E-02	-1.19E-02	-1.15E-02
28	6.57E-02	2.89E-02	-1.44E-02	-1.15E-02
29	7.25E-02	3.42E-02	-1.37E-02	-1.04E-02
30	7.27E-02	3.49E-02	-1.13E-02	-1.13E-02
31	7.45E-02	3.64E-02	-1.01E-02	-1.13E-02
32	7.60E-02	3.76E-02	-9.91E-03	-1.08E-02
34	7.76E-02	3.89E-02	-9.31E-03	-1.07E-02
35	7.77E-02	3.95E-02	-9.50E-03	-1.04E-02
		Rutile		
% hfx	$Ti_c - O$ eq	$Ti_c - O$ ax	$Ti_c - Ti$ eq	$Ti_c - Ti$ ax
20	9.02E-02	1.53E-02	-5.92E-03	-6.24E-02
e5	1.01E-01	1.97E-02	-2.48E-02	-3.23E-02
28	1.03E-01	2.48E-02	-2.85E-02	-2.60E-02
30	1.04E-01	2.57E-02	-2.88E-02	-2.54E-02
35	1.05E-01	2.97E-02	-3.07E-02	-2.02E-02

S 7 HF, MP2 and DH energy difference between $E_{loc,relax}$ = localized charge with a consistent lattice relaxation (polaron) and $E_{loc,perf}$ = localized charge with a perfect (non relaxed) lattice geometry.
The fully delocalized solution $E_{deloc,perf}$ can not be obtained with those methods, due to the high amount of %hfx introduced.
Therefore $E_{pol} = E_{loc,relax} - E_{deloc,perf}$ can not be computed.

	Charge	Geometry
$E_{loc,relax}$ (polaron)	localized	relaxed (polaron distortion)
$E_{loc,perf}$	localized	delocalized (perfect lattice)
$E_{deloc,perf}$	delocalized	delocalized (perfect lattice)

	Anatase $E_{loc,relax} - E_{loc,perf}$ / eV	Rutile $E_{loc,relax} - E_{loc,perf}$ / eV	$\Delta E_{rutile-anatase}$ / eV
HF	-1.03	-1.22	0.19
MP2	-0.63	-0.84	0.21
DH	-0.41	-0.78	0.37

S 8 Polaron formation energies in anatase and rutile, with unit cells of 108 and 216 atoms respectively, computed with hybrid DFT and RPA for varying amounts of %hfx and different starting geometries. Blue= geometry obtained with 25%hfx. Red= geometry obtained with 28%hfx. Green= geometry obtained with 30%hfx. Black= geometry obtained with 35%hfx.



Method	E_{pol} Anatase / eV Starting Polaron Geometry 28	29	30	31	32	33	34	35	40
PBE	0.34	0.42	0.44	0.49	0.50	0.53	0.54	0.55	
trPBE0 (20% hfx)	0.26		0.30			0.35		0.36	
trPBE0 (25% hfx)	0.17	0.18	0.19	0.20	0.20	0.21	0.21	0.21	
trPBE0 (35% hfx)	-0.17	-0.19	-0.19	-0.20	-0.20	-0.20	-0.20	-0.20	
trPBE0 (40% hfx)	-0.39	-0.41	-0.42	-0.43	-0.43	-0.43	-0.44	-0.44	
RPA-PBE	0.28	0.34	0.35	0.39	0.40	0.42	0.43	0.44	
RPA-trPBE0 (20% hfx)	0.00		-0.02			-0.02		-0.01	
RPA-trPBE0 (25% hfx)	-0.12	-0.12	-0.12	-0.12	-0.12	-0.11	-0.11	-0.11	-0.10
RPA-trPBE0 (35% hfx)	-0.21	-0.22	-0.22	-0.22	-0.22	-0.22	-0.22	-0.21	-0.21
RPA-trPBE0 (40% hfx)	-0.23	-0.24	-0.24	-0.24	-0.24	-0.24	-0.24	-0.24	-0.23

Method	E_{pol} Rutile / eV Starting Polaron Geometry 20	25	28	30	35
PBE	0.35	0.40		0.43	0.46
trPBE0 (20% hfx)	-0.25	-0.24	-0.23	-0.23	-0.23
trPBE0 (25% hfx)	-0.55	-0.56	-0.56	-0.55	-0.56
RPA-PBE	-0.70	-0.64		-0.62	-0.57
RPA-trPBE0 (20% hfx)	-0.73	-0.70	-0.68	-0.66	-0.78
RPA-trPBE0 (25% hfx)	-0.71	-0.71	-0.70	-0.69	-0.70

S 9 Computation of the electronic mobilities. T = 300K

$$\text{Adiabatic transfer:} \quad k_{et} = \nu_n exp[\tfrac{-\Delta G^*_{ad}}{k_b T}]$$

$$\text{Nonadiabatic transfer:} \quad k_{et} = \tfrac{2\pi}{\hbar} |V_{ab}|^2 \tfrac{1}{\sqrt{4\pi\lambda k_b T}} exp[\tfrac{-(\lambda^2)}{4\lambda k_b T}]$$

$$\text{In the nonadiabatic limit:} \quad \Delta G^* = \lambda/4$$

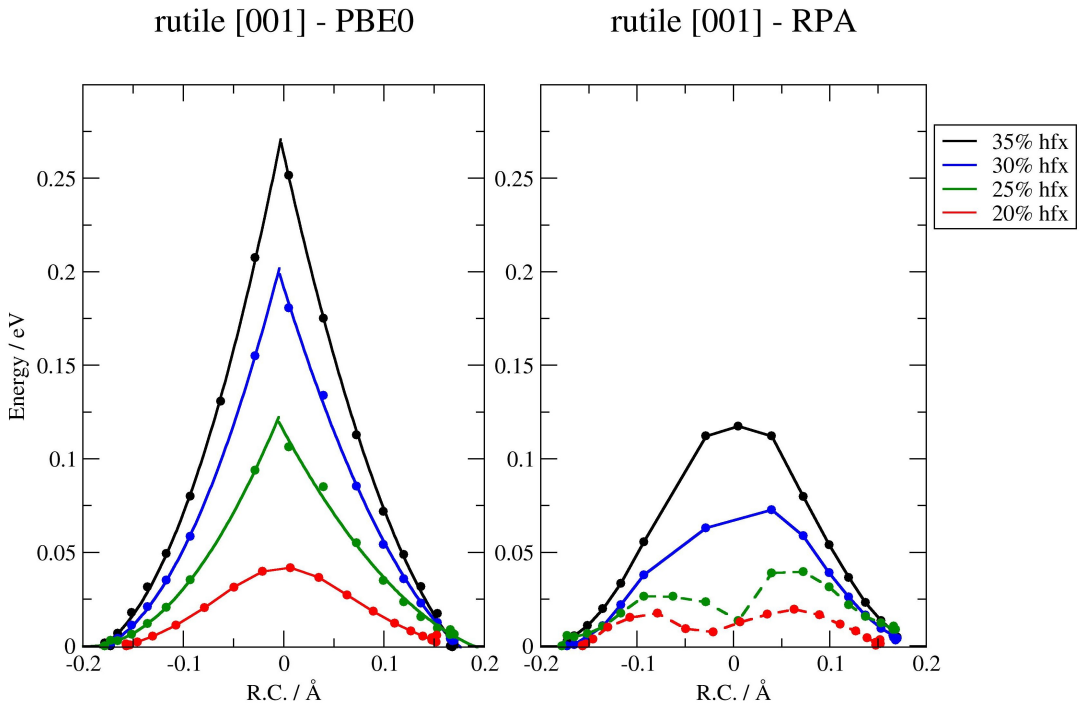
$$D = R^2 n k_{et}$$

$$\mu = \tfrac{eD}{k_b T}$$

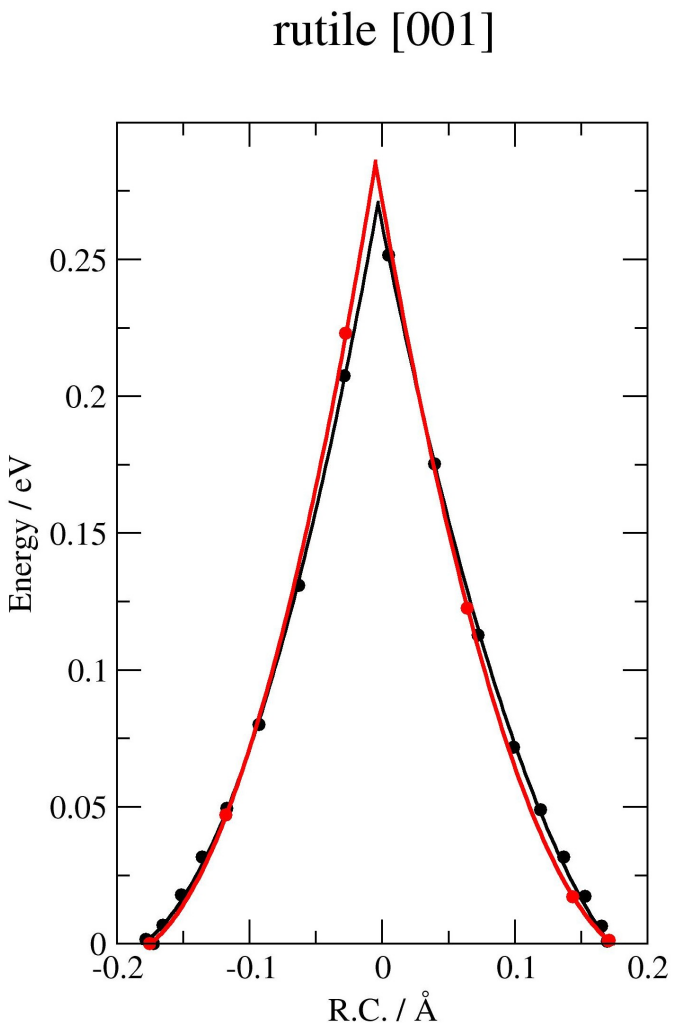
with: ν_n = typical frequency for nuclear motion [8].
V_{AB} = electron coupling element [8].
R = distance between transfer sites
n = number of neighboring electronic accepting sites

Path	R / Å	n
Rutile[001]	2.91	2
Rutile[111]	3.57	8
Anatase[100]	3.03	4
Anatase[201]	3.78	4

S 10 Comparison of the NEB profiles for the [001] electron hopping in rutile, computed with the truncated PBE0 functional and RPA, at different amounts of %hfx. Dashed lines indicate profiles affected by RPA overcorrelation.



S 11 NEB profiles for the [001] electron hopping in rutile, with the truncated PBE0 functional (35% hfx). Black: $3 \times 3 \times 4$ system, 216 atoms. Red: $3 \times 3 \times 4$ system,1728 atoms.



S 12 .Example of CP2K input file for RPA-trPBE0(25% hfx) calculations, with all the relevant simulation parameters

```
&FORCE_EVAL
    METHOD Quickstep
  &DFT
    &MGRID
      CUTOFF 600
    &END MGRID
    &QS
      EPS_DEFAULT 1.0E-12
      EXTRAPOLATION_ORDER 3
    &END QS
    &SCF
      EPS_SCF 1.0E-8
      &OUTER_SCF
        EPS_SCF 1.0E-8
      &END
      &OT
         ENERGY_GAP 0.01
      &END OT
    &END SCF

    &XC
      &XC_FUNCTIONAL
        &PBE
           SCALE_X 0.75
           SCALE_C 1.0
         &END
         &PBE_HOLE_T_C_LR
           CUTOFF_RADIUS 4.5
           SCALE_X 0.25
         &END
      &END XC_FUNCTIONAL
      &HF
        &INTERACTION_POTENTIAL
          POTENTIAL_TYPE TRUNCATED
          CUTOFF_RADIUS 4.5
        &END
        FRACTION 0.25
        &SCREENING
          EPS_SCHWARZ              1.0E-9
        &END
      &END HF
      &WF_CORRELATION
        METHOD  RI_RPA_GPW
        &RI_RPA
          RPA_NUM_QUAD_POINTS   100
          &HF
            FRACTION  1.0
            &SCREENING
              EPS_SCHWARZ           1.0E-9
              SCREEN_ON_INITIAL_P  TRUE
            &END SCREENING
            &INTERACTION_POTENTIAL
              POTENTIAL_TYPE TRUNCATED
              CUTOFF_RADIUS  4.5
            &END
          &END HF
        &END
      &END XC
  &END DFT

  &SUBSYS
   &KIND O
      BASIS_SET cc-TZ
      RI_AUX_BASIS_SET RI_TZ
      POTENTIAL GTH-PBE-q6
    &END KIND
    &KIND Ti
      BASIS_SET cc-TZ
      RI_AUX_BASIS_SET cc-TZ
      POTENTIAL GTH-PBE-q12
    &END KIND
  &END SUBSYS
&END FORCE_EVAL
```

S 13 CC, RI, ADMM and *all electron Basis Sets for Ti and O*

```
O  cc-TZ
  6
  2  0  1  3  1  1
       10.2674419938   0.0989598460  -0.0595856940
        3.7480495696   0.1041178339  -0.1875649045
        1.3308337704  -0.3808255700  -0.3700707718
  2  0  1  1  1  1
        0.4556802254   1.0000000000   1.0000000000
  2  0  1  1  1  1
        0.1462920596   1.0000000000   1.0000000000
  3  2  2  1  1
        2.3140000000   1.0000000000
  3  2  2  1  1
        0.6450000000   1.0000000000
  4  3  3  1  1
        1.4280000000   1.0000000000
#
TI cc-TZ
 10
 2 0 0 3 2
   3.7986698150634766E+00  -1.0531476885080338E-01  -6.8273013830184937E-01
   1.9114010334014893E+00   2.1265093982219696E-01   6.9480454921722412E-01
   7.5023883581161499E-01  -9.7143632173538208E-01   2.6111095011234283E-01
 2 0 1 1 1 1
   0.3   1.0 1.0
 2 0 1 1 1 1
   0.2   1.0 1.0
 2 0 2 1 1 1 1
   0.13  1.0 1.0 1.0
 2 1 1 3 1
   9.4607772827148438E+00  -9.9228985607624054E-02
   1.8190858364105225E+00   6.7078214883804321E-01
   7.1252536773681641E-01   7.3498630523681641E-01
 2 2 2 3 1
   5.8364233970642090E+00   2.9940614104270935E-01
   2.2766182422637939E+00   5.6059896945953369E-01
   9.0494173765182495E-01   7.7206534147262573E-01
 2 2 2 1 1
   3.6325827240943909E-01   1.0
 2 3 3 1 1
   1.2482999563217163E+00   1.0
 2 3 3 1 1
   2.8360000252723694E-01   1.0
 2 4 4 1 1
   7.2509998083114624E-01   1.0
#
```

```
#
 O   RI
  20
  1  0  0  1  1
       24.5595006061        1.0000000000
  1  0  0  1  1
        8.3254503805        1.0000000000
  1  0  0  1  1
        2.8895585562        1.0000000000
  1  0  0  1  1
        1.3383587201        1.0000000000
  1  0  0  1  1
        0.8797495165        1.0000000000
  1  0  0  1  1
        0.2902204697        1.0000000000
  1  1  1  1  1
       15.0341204959        1.0000000000
  1  1  1  1  1
        3.9838033442        1.0000000000
  1  1  1  1  1
        2.2151496463        1.0000000000
  1  1  1  1  1
        0.8979637674        1.0000000000
  1  1  1  1  1
        0.4128471304        1.0000000000
  1  2  2  1  1
       15.8683289847        1.0000000000
  1  2  2  1  1
        5.3913486662        1.0000000000
  1  2  2  1  1
        2.5385447175        1.0000000000
  1  2  2  1  1
        1.0911199995        1.0000000000
  1  2  2  1  1
        0.3766843343        1.0000000000
  1  3  3  1  1
        4.6812603411        1.0000000000
  1  3  3  1  1
        2.1656106741        1.0000000000
  1  3  3  1  1
        1.0331835741        1.0000000000
  1  4  4  1  1
        2.3079719899        1.0000000000
#
O ADMM
 5
 1  0  0  1  1
 0.27061 1.0
 1  0  0  2  1
 0.88493 1.0
 8.50409 -0.23485406547006335010
 1  1  1  1  1
 0.31040 1.0
 1  1  1  2  1
 1.38256 1.0
 6.08264 0.34108818521609718388
 1  2  2  1  1
 1.00000000          1.00000000
#
```

```
Ti   RI
 34
   1   0   0   1   1
    9.8703935249    1.0000000000
   2   0   0   1   1
    5.3949794100    1.0000000000
   3   0   0   1   1
    2.7086611925    1.0000000000
   4   0   0   1   1
    1.8082742275    1.0000000000
   5   0   0   1   1
    1.0801564940    1.0000000000
   6   0   0   1   1
    0.7584164945    1.0000000000
   7   0   0   1   1
    0.4045769082    1.0000000000
   8   0   0   1   1
    0.1330852528    1.0000000000
   9   1   1   1   1
    8.1808558939    1.0000000000
  10   1   1   1   1
    4.5538321857    1.0000000000
  11   1   1   1   1
    2.7521196163    1.0000000000
  12   1   1   1   1
    1.6446789196    1.0000000000
  13   1   1   1   1
    0.9542861525    1.0000000000
  14   1   1   1   1
    0.6028776093    1.0000000000
  15   1   1   1   1
    0.3343917702    1.0000000000
  16   1   1   1   1
    0.1787815275    1.0000000000
  17   2   2   1   1
    7.9133457786    1.0000000000
  18   2   2   1   1
    3.4989438788    1.0000000000
  19   2   2   1   1
    1.6217483065    1.0000000000
  20   2   2   1   1
    0.7728081912    1.0000000000
  21   2   2   1   1
    0.4387679132    1.0000000000
  22   2   2   1   1
    0.2146775819    1.0000000000
  23   3   3   1   1
    4.4157045752    1.0000000000
  24   3   3   1   1
    1.8006904504    1.0000000000
  25   3   3   1   1
    1.1570683357    1.0000000000
  26   3   3   1   1
    0.6099266869    1.0000000000
  27   3   3   1   1
    0.3727449239    1.0000000000
  28   4   4   1   1
    4.2120733320    1.0000000000
  29   4   4   1   1
    1.9995398809    1.0000000000
  30   4   4   1   1
    0.9095934373    1.0000000000
  31   4   4   1   1
    0.4436121782    1.0000000000
  32   5   5   1   1
    1.9719657313    1.0000000000
  33   5   5   1   1
    0.8502189480    1.0000000000
  34   6   6   1   1
    1.1815873138    1.0000000000
```

```
#
TI ADMM
           11
            2           0           0           1           1
    4.0993528      0.99999994
            2           0           0           1           1
    1.3253083      0.99999994
            2           0           0           1           1
   0.54136300      0.99999994
            2           0           0           1           1
   0.10175999      0.99999994
            2           1           1           1           1
    8.9996204      0.99999994
            2           1           1           1           1
    1.6365473      0.99999994
            2           1           1           1           1
   0.54614919      0.99999994
            2           2           2           1           1
    3.6633232      0.99999994
            2           2           2           1           1
   0.88037348      0.99999994
            2           2           2           1           1
   0.23061574      0.99999994
            2           3           3           1           1
   0.49442869      0.99999994
#
#
# O_8-411d1_cora_2005 : crystal
O all
5
1 0 0 8 1
 8020.0 0.00108
 1338.0 0.00804
 255.4 0.05324
 69.22 0.1681
 23.90 0.3581
 9.264 0.3855
 3.851 0.1468
 1.212 0.0728
1 0 1 4 1 1
 49.43 -0.00883 0.00958
 10.47 -0.0915 0.0696
 3.235 -0.0402 0.2065
 1.217 0.379 0.347
1 0 1 1 1 1
 0.500 1.0 1.0
1 0 1 1 1 1
 0.191 1.0 1.0
1 2 2 1 1
 0.500 1.0
#
#
```

```
#
# Ti Ti_86-411(d31)G_darco_unpub : crystal
Ti all
7
1 0 0 8 1
 225338.0 0.000228
 32315.0 0.001929
 6883.61 0.011100
 1802.14 0.05
 543.063 0.17010
 187.549 0.369
 73.2133 0.4033
 30.3718 0.1445
1 0 1 6 1 1
 554.042 -0.0059 0.0085
 132.525 -0.0683 0.0603
 43.6801 -0.1245 0.2124
 17.2243 0.2532 0.3902
 7.2248 0.6261 0.4097
 2.4117 0.282 0.2181
1 0 1 4 1 1
 24.4975 0.0175 -0.0207
 11.4772 -0.2277 -0.0653
 4.4653 -0.7946 0.1919
 1.8904 1.0107 1.3778
1 0 1 1 1 1
 0.8099 1.0 1.0
1 0 1 1 1 1
 0.3242 1.0 1.0
1 2 2 3 1
 7.6781 0.1127
 1.8117 0.3927
 0.463 0.5206
1 2 2 1 1
 0.23 1.0
```

References

1 J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson and J. V. Smith, *J. Am. Chem. Soc.*, 1987, **109**, 3639–3646.
2 Y. M. Niquet and X. Gonze, *Phys. Rev. B*, 2004, **70**, 245115.
3 L. Chiodo, J. M. García-Lastra, A. Iacomino, S. Ossicini, J. Zhao, H. Petek and A. Rubio, *Phys. Rev. B*, 2010, **82**, 045207.
4 The CP2K developers group, www.cp2k.org.
5 T. Bredow, P. Heitjans and M. Wilkening, *Phys. Rev. B*, 2004, **70**, 115111.
6 F. Corá, *Molecular Physics*, 2005, **103**, 2483–2496.
7 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, *Journal of Physics: Condensed Matter*, 2009, **21**, 395502.
8 N. A. Deskins and M. Dupuis, *Phys. Rev. B*, 2007, **75**, 195212.